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Analysis of the Barrier Properties of Polyimide-Silicate Nanocomposites

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ANALYSIS OF THE BARRIER PROPERTIES OF POLYIMIDE-SILICATE NANOCOMPOSITES

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ABSTRACT

Montmorillonite clay was organically modified and dispersed into a thermoplastic (BPADA-BAPP) and a thermosetting (PMR-15) polyimide matrix. The barrier properties of the neat resins and the nanocomposites were evaluated. Reductions in gas permeability and water absorption were observed in thermoplastic polyimide nanocomposites. The thermosetting polyimide showed a reduction in weight loss during isothermal aging at 288 °C. Carbon fabric (T650-35, 8 HS, 8 ply) composites were prepared using both the BPADE-BAPP and PMR-15 based nanocomposites. Dispersion of the layered silicate in the BPADA-BAPP matrix reduced helium permeability by up to 70%. The PMR-15/ silicate nanocomposite matrix had an increase in thermal oxidative stability of up to 25%.

1. INTRODUCTION

It is well known that the dispersion of a layered silicate into a polymer matrix can dramatically decrease gas permeation through the polymer. Therefore, polymer nanocomposites offer potential in the development of lightweight, durable LH2 tankage for use in a wide range of applications from reusable launch vehicles to fuel cell powered aircraft. Nanocomposites also offer potential in the development of polymer matrix composites for high temperature aero-space propulsion applications.

Polymer matrix composites have several advantages for cryogenic storage tanks. They are lightweight, strong and stiff, so a smaller fraction of a vehicles potential payload capacity is used for propellant storage. Unfortunately, the resins typically used to make PMC tanks have higher gas permeability than metals, which can lead to hydrogen loss through the body of the tank. One approach to eliminate this problem is to build composite tanks with thin metal liners. While this reduces hydrogen permeability, it can introduce problems due to the substantial mismatch in the

coefficient of thermal expansion. Polymer-silicate nanocomposites can reduce the hydrogen permeability through the composite, without introducing a CTE mismatch, offering the potential for the development of linerless PMC tanks.

The decrease in gas permeability is also important for high temperature applications. It has been shown that the main route to the degradation of PMR-15 is through oxidation. Isothermal aging in air results in a surface layer of oxidized polymer, which cracks with further aging. Cracking within the oxidation layer increases the surface area available for oxidation and allows permeation of oxygen into the bulk of the sample, furthering oxidative degradation.[1] Dispersion of the silicate in the polymer should decrease permeation of oxygen into the composite, thereby enhancing thermal stability.

2. EXPERIMENTAL

2.1 Materials Montmorillonite (PGV-grade, CEC = 145 meq/100g) was received from Nanocor and will be referred to as PGV. Bentonite (Bentolite-H, CEC = 90 meq/100g) was received from Southern Clay Products, and will be referred to as SCP. Ion exchange amines: methylene dianiline (MDA) and dodecylamine (C12) were purchased from Aldrich. 2-carbomethoxy-3-carboxy-5-norbornene (NE) and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) were purchased from Christev. Bisphenol-A dianhydride (BPADA) was purchased from GE plastics, and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) was purchased from the Wakayama Seika Kogyo company. All materials were used in the as-received condition.

2.2 PMR-15 Synthesis BTDE was prepared by refluxing BTDA in an amount of methanol calculated to yield a solution containing 50 wt% solids. The reflux was carried out for two hours after the solid BTDA had dissolved. Dissolution indicates the formation of the acid ester (BTDE) species.[2] The solution was used immediately for resin synthesis.

PMR-15 resins were fabricated in several steps. The three monomers (BTDE, MDA, and NE) were dissolved in methanol (50 wt%) followed by solvent evaporation, on a hot plate, at 60 to 70 °C. B-staging the mixture at 204 to 232 °C in an air circulating oven produced low molecular weight imide oligomers. The oligomers were then cured in a mold at 315 °C under 2355 psi to produce the crosslinked polymer. The polymer was post cured in an air circulating oven for 16 hours at 315 °C to further crosslinking. The average number of imide rings was kept constant by using a stoichiometry of 2NE/ (n + 1)MDA/ nBTDE (n = 2.087) corresponding to an average molecular weight of 1500.

2.3 BPADA-BAPP Synthesis The polyimide was prepared by stirring a 20 wt% solids solution of BPADA and BAPP in dry NMP overnight at room temperature. The solution was then refluxed for four hours, allowed to cool, and the resulting polymer was precipitated by addition to ethanol. The precipitate was then dried, dissolved in dichloromethane, and precipitated a second time.

2.4 BPADE-BAPP Synthesis The acid-ester of BPADA was prepared by refluxing the dianhydride in an amount of methanol calculated to yield a solution containing 50 wt% solids. The reflux was carried out for two hours after the solid BPADA had dissolved. Dissolution indicates the formation of the acid ester (BPADE) species. The solution was used immediately for resin synthesis.

The polyimide was fabricated in several steps, as illustrated in Figure 1. A 1:1 mixture of monomers (BPADE and BAPP) was dissolved in methanol (50 wt%) followed by solvent evaporation, on a hot plate, at 60 to 70 °C. B-staging the mixture at 204 to 232 °C in an air circulating oven produces the amic acid. The amic acid is then imidized in a mold at 232 °C under 500 psi to produce the polymer.

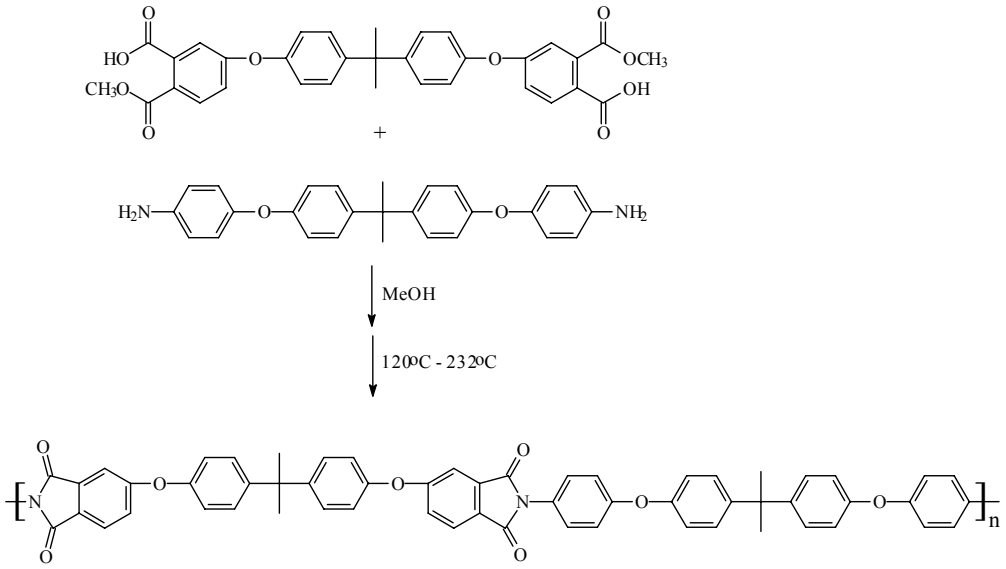

Figure 1. Synthesis of BPADE-BAPP.

2.5 Nanocomposite Synthesis Ion exchange of the interlayer cations of silicate with the protonated forms of the MDA and/or C12 was performed by dissolving the amine (5mmol) in 450 mL of a 0.005M aqueous HCl solution at 60 °C. For co-exchange of MDA with C12, 2.5 mmol of each amine was added to the 0.005M aqueous HCl solution. The silicate (5g) was dispersed in the solution and the resulting mixture was stirred at 60 °C for three hours. The solution was filtered and the clay was washed thoroughly with warm (60 °C) distilled water. To maximize the amount of diamine exchanged, this procedure was repeated for a total of three exchange reactions.[3] The silicate was then dried overnight in a vacuum oven at 100 °C. PGV ion exchanged with MDA and C12 was added to the PMR-15 matrix, and will be referred to as PGV(MDA/C12). Bentonite-H, ion exchanged with C12, was dispersed in the thermoplastic polyimide, and will be referred to as SCP12.

2.6 Carbon Fabric Reinforced Polyimide Carbon fabric reinforced composites were prepared with a PMR-15/ silicate nanocomposite matrix. Prepreg was prepared by brush application of the PMR-15 monomer solution onto T650-35 carbon fabric, to give a final fiber content of

60 wt%. The prepreg sheets were cut into eight, 10.2 cm by 10.2 cm, plies and placed in a metal mold. The mold was heated to 204 °C for 1 hour and 232 °C for 0.5 hours, to produce low molecular weight imide oligomers. The mold temperature was then raised to 315 °C, and the matrix was cured with application of 500 psi for 2 hours. The composites were post cured in an air circulating oven at 315 °C for 16 hours. A BPADE/BAPP/ silicate matrix composite was prepared following this same procedure, except that the sample was processed at 288 °C for 1.5 hours at 500 psi.

2.7 Characterization X-ray diffraction (XRD) patterns were obtained using a Philips XRG 3100 X-ray diffractometer with Ni-filtered CuKα radiation. Ion exchanged clays and polymer nanocomposites were ground into powder and the XRD data was recorded in the range of $2\theta = 2$ to 32°. An increase in the basal layer spacing, which was determined from a shift in the (001) peak position, indicates ion exchange or polymer intercalation between the silicate layers. Disappearance of the (001) peak suggests an exfoliated morphology.

Transmission electron microscopy (TEM) specimens were prepared by microtoming sections of the polymer nanocomposites, 20 to 70 nm thick, and floating the sections onto Cu grids. Micrographs were obtained with a Philips CM 200, using an acceleration voltage of 200 kV.

Isothermal aging of the PMR-15 nanocomposites was performed to determine their TOS. Post-cured samples were cut into 1.02 cm by 0.64 cm coupons and placed in an air circulating oven at 288 °C for 1000 hours. The weight loss was measured at regular intervals by removing the coupons from the oven, cooling to room temperature in a desiccator, and weighing the sample.

Ultrasonic scanning (C-scan) was used to characterized the composite quality. Void content was measured by acid digestion, in accordance with ASTM Standard D792.

Helium permeability of the thermoplastic polyimide matrix composites was performed by Northrop Grumman. Hydrogen permeability data was provided by Southern Research Institute.

Flexural strength, flexural modulus, and interlaminar shear strength of carbon fabric reinforced composites were measured using an Instron Model 4505 with Series IX acquisition software. A 3- point flexure test, ASTM D790, was used to evaluate flexural strength and modulus. Short beam shear tests followed ASTM D2344, for measurements of interlaminar shear strength. Values are an average of six samples.

3. RESULTS AND DISCUSSION

The level of dispersion of the organically modified layered silicate was investigated by XRD and TEM. The TEM images depicting the dispersion of 2 wt% of an organically modified silicate in a BPADA-BAPP, BAPDE-BAPP and a PMR-15 matrix are shown in Figures 2a, 2b, and 2c respectively. The layer separation in the BPADA-BAPP sample suggests intercalation of the polymer between the clay layers, but overall good dispersion of the clay. An exfoliated morphology was obtained in the thermoplastic matrix nanocomposites prepared from BPADE, rather than BPADA. The silicate layers were well dispersed in the polymer and there was no

evidence of residual structural registry. Dispersion of the layered silicate in the PMR-15 matrix was more difficult. Typically, an intercalated nanocomposite morphology was obtained, although there were regions where the order of the silicate layers was highly disrupted.

3.1 BPADA-BAPP nanocomposites Hydrogen permeability measurements of the neat polymer and the nanocomposites revealed a 20% decrease in hydrogen permeability upon addition of 2 wt% of B12. Water absorption was also decreased by approximately 20%, as illustrated in Figure 3. The reduction in permeability through a nanocomposite has been attributed to the increased distance that a gas molecule must to travel when the silicate platelets are dispersed in the matrix.[4] This "tortuosity factor" has been modeled[5] and it is clear that an exfoliated morphology, and alignment of the platelets normal to the direction of permeation will give the maximum reduction in permeability. Simply compression molding the polymer results in a random orientation of the silicate particles, therefore the enhancement in barrier properties is typically near 20%. Further reductions in permeability could be achieved by alignment of the silicate platelets.

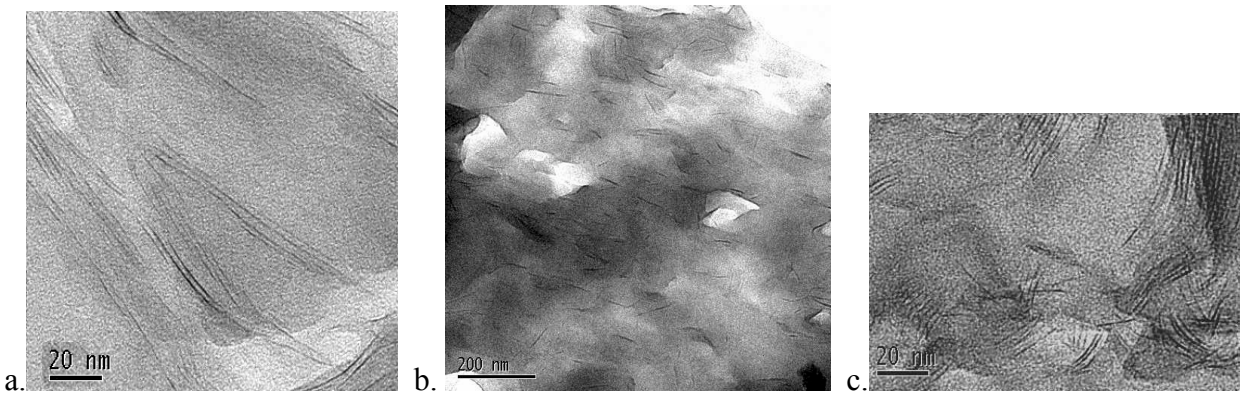

Figure 2. TEM image of: a. 2 wt% SCP12 in BPADA-BAPP, b. 2 wt% SCP12 in BPADE-BAPP, and c. 2 wt% PGV(MDA-C12) in PMR-15.

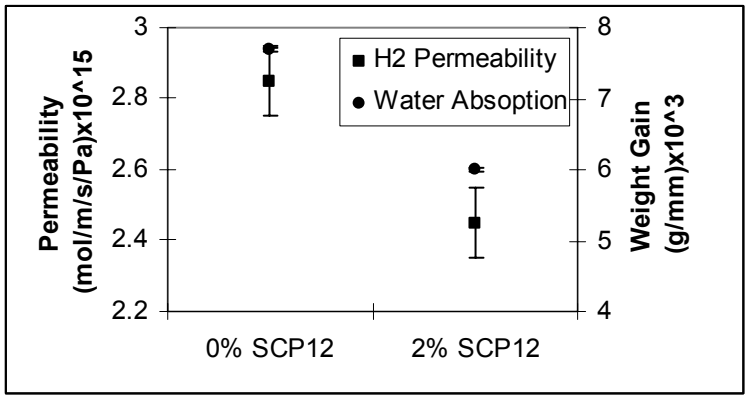

Figure 3. Hydrogen permeability and water absorption in BPADA-BAPP.

3.2 Carbon fabric reinforced composites Preparation of carbon fabric reinforced composites required preparation of the polyimide from the diacid-diester of BPADA. TEM analysis of the BPADE-BAPP nanocomposites, in the absence of carbon fabric reinforcement, resulted in highly dispersed silicate layers. The nanocomposite morphology of the carbon fabric reinforced samples was not analyzed by TEM because sample preparation was difficult. Instead, a section of the composite was mounted in epoxy, with the composite cross section exposed. Optical microscopy of these composites provides an indication of the size scale on which the silicate is dispersed. Figure 4a shows the cross section of a composite prepared with a neat resin matrix. Figure 4b shows a nanocomposite matrix containing 2 wt% B12. The lack of visible clay particles suggests that layer dispersion is on the nanometer level. For comparison, Figure 4c shows a BPADE/BAPP matrix containing 2 wt% of clay, organically modified with protonated BAPP. In this case, the large agglomerates of the silicate are visible, indicating poor dispersion of this clay.

The helium permeability of carbon fabric reinforced composites was measured, as shown in Figure 5. Hydrogen permeability testing is currently underway. In the nanocomposite matrix composites, dispersion of 2 wt% B12 reduces the gas permeability by up to 70%, compared to that of the neat resin matrix composite. This is significantly larger than the change in permeability seen in the neat resin nanocomposite. This large decrease in the permeability of the nanocomposite matrix composite suggests that the carbon fibers may align the silicate layers, thereby increasing the path a diffusing gas must travel. Measurements of the mechanical properties of these composites show an increase in modulus, but no change in flexural strength or interlaminar shear strength.

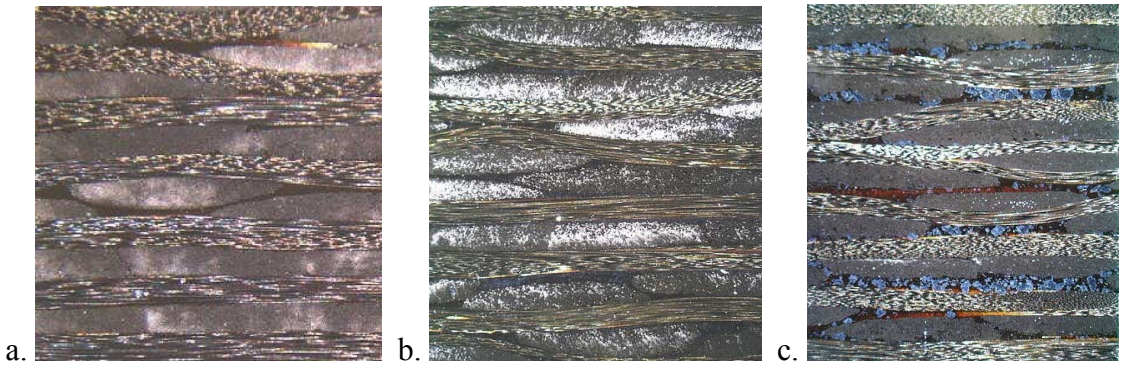

Figure 4. Optical microscopy images of: a. BPADE-BAPP matrix composite, b. BPADE-BAPP matrix composite containing 2 wt% SCP12, and c. BPADE-BAPP matrix composite containing 2 wt% SCP modified with BAPP.

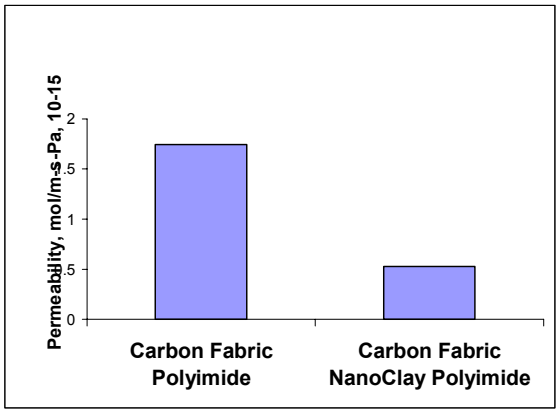

Figure 5. Helium permeability of BPADE-BAPP matrix composites.

3.3 Characterization of PMR-15 nanocomposites The thermal oxidative stability of PMR-15 nanocomposites has been reported.[6] The addition of 5 wt% PGV(MDA-C12) results in a 15% reduction in weight loss after aging for 1000 hours at 288 °C. These results were also observed in this work. Figure 6 shows the weight loss of the neat resin and the nanocomposite aged in air and under nitrogen. While the weight loss of all samples aged in nitrogen was lower than those aged in air, in each case, addition of clay reduced weight loss by 15%.

A greater decrease in weight loss is obtained for carbon fabric reinforced composites. Dispersion of only 1 or 2 wt% clay decreases the weight loss on oxidative aging by 25 and 20%, respectively. The improvements with such a small amount of silicate may be attributed to the greater dispersion of smaller amounts of clay. Optical microscopy (Figure 7) shows that agglomeration of the clay particles occurs at increased clay concentration (> 2 wt%).

Optical microscopy images also revealed more cracking in the neat resin matrix composite than in the nanocomposite. This would account for the greater weight loss on aging.

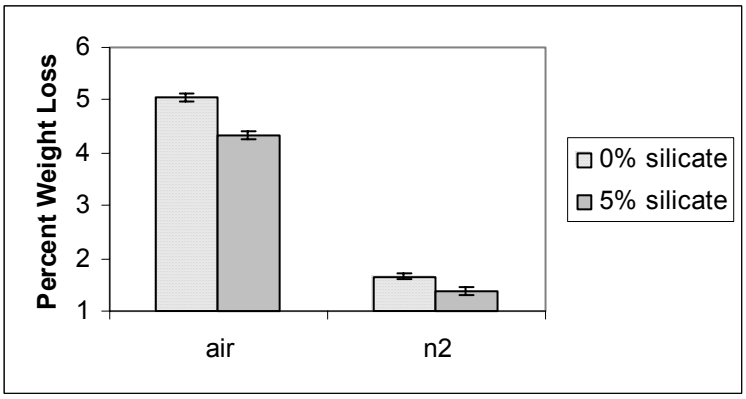

Figure 6. Weight loss on aging PMR-15 for 940 hours at 288 °C, in air and nitrogen.

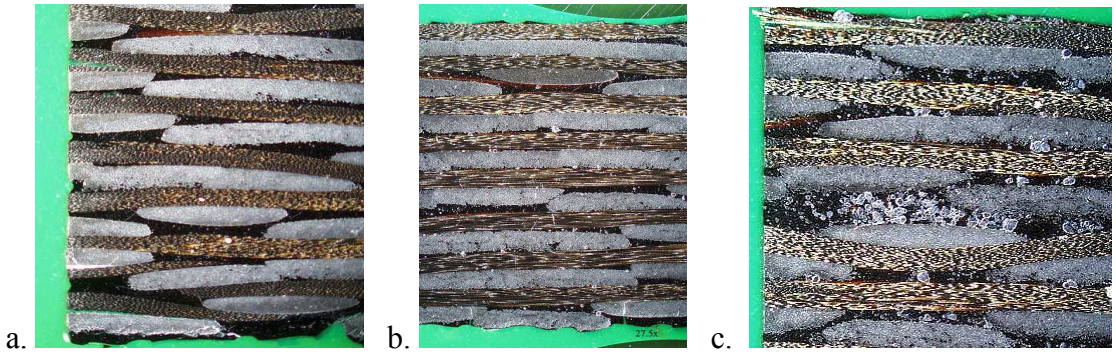

Figure 7. Optical microscopy images of PMR-15 matrix composites aged for 1000 hours at 288 °C. The composites contain, a. 0 wt% silicate, b. 1 wt% silicate, and c. 5 wt% silicate.

4. CONCLUSIONS

Dispersing low concentrations of a layered silicate can improve the barrier properties of the polymer. The gas permeability through the thermoplastic matrix was greatly decreased in the presence of carbon fabric reinforcement. The high temperature oxidative stability of the carbon fabric reinforced nanocomposites was also enhanced. The data suggests that the carbon fibers may aid in aligning the silicate layers.

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13. ABSTRACT ***(Maximum 200 words)***

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